NANOTUBE ENGINEERING

Final Report

JPL Task 935

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A. OBJECTIVES

Carbon nanotubes exhibit a variety of unique properties, which make them well suited for state-of-the-art sensor applications of interest to NASA. This effort focused on nanotube growth and device processing development aimed at nanotube device applications, including a novel biomimetic acoustic sensor modeled after the rod-like stereocilia arrays that provide the hearing mechanism for all mammals. The major objectives of this work were to develop the growth and processing techniques for producing uniform carbon nanotube arrays, and to utilize these arrays to demonstrate the basic concept of acoustic sensing with artificial stereocilia. The baseline process for producing uniform nanotube arrays utilized alumina nanopores as a template for growth of hexagonally ordered arrays, but complementary processes for fabrication of arrays with more complex ordering were also developed.

B. PROGRESS AND RESULTS

1. Alumina pore array development

It has been known for decades that anodic oxidation of aluminum results in the formation of long, straight nanopores with diameters less than 100 nm, and aspect ratios that can exceed 500:1. More recently it has been found that careful control of the anodization process can produce highly ordered arrays of nanopores. Both Brown University and Caltech contributed to optimization of the alumina nanopore process under this program. The alumina nanopore structures can be used as templates for growth of carbon nanotubes (CNT) by electrodepositing Co in the bottom of the nanopores and using chemical vapor deposition (CVD) with acetylene. Prof. Xu's group at Brown has used this process to grow high quality multiwall carbon nanotubes in the pores. Following nanotube growth, the alumina matrix is etched back using a mixture of phosphoric and chromic acid or Ar ion milling to expose the ends of the nanotubes as shown in Figure 1a) for an ion-etched sample. The exposed nanotubes in Fig.1a) are less than 200 nm long. However, the biomimetic acoustic sensor and other applications of interest require tubes greater than ~500 nm in length. Wet etching of the alumina can produce longer exposed nanotubes, but it has been found that nanotubes with large aspect ratios tend to clump and stick in this process as shown in Fig. 1b). Recently, Prof. Xu's group has found that they can significantly reduce the nanotube sticking problem by adding suitable dispersants to the wet etching solution as indicated in Fig. 1 c). This is a very promising result that Prof. Xu will pursue in collaboration with this team under new funding from DARPA aimed at demonstration of CNT high-Q mechanical oscillators.

2. Nanotube growth and array processing

As part of this program, we developed a nanotube growth process at JPL which uses plasma-enhanced (PE) CVD in an ethylene/hydrogen atmosphere to produce carbon nanotubes at temperatures ranging from 410-750°C. The nanotube growth is selectively nucleated on a variety of thin metal catalysts, including a new Ti/Ni bilayer developed in our group. Figure 2a) illustrates the dense vertically-aligned arrays that are produced on the metal catalyst films using the ethylene CVD process at 635°C. However, closer inspection of the nanotubes reveals that the tubes show local bending, which is a sign of defect incorporation during growth. This finding motivated the development of a high temperature CVD process using a new tube-furnace-based system capable of growth above 1000°C. Figure 2c) shows a recent example of CNT growth using methane CVD in this system at 900°C. In this case, it was found that an unpatterned sub-nm Fe catalyst layer produced a sparse array of straight, freestanding vertical and off-vertical nanotubes. The important points to note are that the tubes are very straight, which indicates a low defect density, and that the tubes are sticking up from the substrate surface. This geometry is ideal for our acoustic sensor application as well as other CNT-based devices.

Because the nanotubes grow only on areas of the substrate with catalyst material present, it should be possible to produce ordered arrays of such freestanding nanotubes by patterning arrays of catalyst dots with diameters on the order of 20-30 nm using electron beam lithography (EBL) or alternate techniques. The e-beam approach has the advantage of flexibility in pattern design, but is also pushing the resolution limits of EBL and is expensive to implement. Figure 3 shows a number of catalyst patterns defined using the new JEOL EBL system in the Microdevices laboratory at JPL. Fig. 3a) shows Fe catalyst dots ~50 nm in diameter, while Fig. 3b) and 3c) are images of 30 nm pores patterned by EBL and RIE and then partially filled with Fe catalyst layers. We have grown carbon nanotubes from samples similar to that shown in Fig. 3a) using our low temperature PECVD process, but these nanotubes exhibited the type of defective growth seen in Fig. 2b). Higher temperature nanotube growth using methane at 900°C was attempted with the pore catalyst samples of Fig. 3b) and 3c), but was not successful in the initial runs. We believe the growth did not occur because the Fe catalyst thickness must be re-optimized for the pore geometry. This optimization will be pursued under new programs from NASA Code R and DARPA. We also started investigations of a much different approach for patterning catalyst dot arrays, which utilizes self-organizing block copolymers (Bronikowski and Hunt, NTR, 2001). The great advantage of the block copolymer approach is that it should be able to quickly and efficiently define large areas of ordered nanotubes for a variety of practical applications. This process has been used to pattern 10-30 nm Mo dots for nanotube growth. The growth studies are proceeding with the new funding sources mentioned, as well as under a DRDF focused on this approach (M. Bronikowski, 2002).

3. Development of acoustic readout techniques of nanotube arrays

Experiments were started to determine the acoustic response of dense nanotube arrays such as those shown in Figure 2a). The main approach to date has utilized an Environmental Scanning Electron Microscope (ESEM) to directly visualize the response of the nanotube arrays to an acoustic input provided by flowing gas. The results indicate that the sparser arrays generated by the nanopore or EBL approaches will be essential for high performance acoustic

sensors. We have obtained ASTID funding to continue development of the CNT acoustic sensors (Noca).

C. SIGNIFICANCE OF RESULTS

This task has developed improved techniques for nanotube array fabrication, including improvements in the anodized alumina nanopore process, demonstration of nm scale catalysts defined by electron beam lithography, and a new process using self-assembling block copolymer arrays. The funding for this program also enabled the development of a CMOS-compatible plasma-enhanced CVD process and an improved high temperature CVD process for growth of low-defect-density freestanding nanotubes. The techniques developed here for production of uniform nanotube arrays are expected to be useful for a variety of applications above and beyond the biomimetic acoustic sensor, including biomolecular separation (e.g. DNA sequencing), biomolecular sensing, and mechanical signal processing. The progress made in this seed effort and in complementary programs has already led to follow-on funding from DARPA in a new program aimed at using carbon nanotubes for high-Q resonators for signal processing applications ($2.3M over 3 years, starting 10/01). We have also obtained new funding from the ASTID program for nanotube-based acoustic sensors ($230K, 1 year), and the NASA Code R BioNano program for development of carbon and Si nanowire biosensors ($1.3M over 3 years).

D. FINANCIAL STATUS

The total funding for this task was $110,000, all of which has been expended.

E. PERSONNEL

In addition to the people listed on the title page, other personnel active in this effort include Mike Bronikowski, Dan Choi, Bob Kowalczyk, and Roger Williams.

F. PUBLICATIONS AND PRESENTATIONS

[1] B.D. Hunt, F. Noca, M. Hoenk, “Carbon Nanotube Actuators And Force Sensors,” NASA NTR, NPO-21153. (9/00), Patent application, 1/02.

[2] B.D. Hunt, D. Choi, M. Hoenk, R. Kowalczyk, F. Noca, “Pattern-Aligned Carbon Nanotube Growth,” NASA NTR, NPO-30205 (3/01), Patent application 4/02.

[3] B.D. Hunt, F. Noca, M. Hoenk, “A Carbon Nanotube Tunable High-Q Resonator And Spectrum Analyzer,” NASA NTR, NPO-30206 (3/01), Patent application 4/02.

[4] D. Hoppe, B.D. Hunt, M. Hoenk, F. Noca, J. Xu, “Waveguide-Embedded Carbon Nanotube Array RF Filter and RF Filter Bank,” NASA New Technology Report, NPO-30207 (3/01), Patent application 4/02.

[5] M. Bronikowski and B.D. Hunt, “Regular arrays of carbon nanotubes produced using templates from nano-structured block-copolymeric materials,” NASA New Technology Report, NPO-30240 (5/01).

[6] F. Noca et al., "Nanotube-Based Sensors and Systems for Outer Planetary Exploration," Outer Planetary Exploration Workshop, Houston, 2/21/00.

[7] M. Hoenk et al., "Carbon-Nanotube-Based Sensors and Systems," Nanospace 2001, Galveston, TX, March 13-16, 2001.
[8] *Invited: M. Bronikowski, "Carbon nanotube growth by HiPCO process," APS March Meeting, 3/01, Seattle.
[9] B.D. Hunt et al., “Nanomechanical Resonators Based on Carbon Nanotubes,” Nanoscale/ Molecular Mechanics Meeting, Maui, Hawaii, 5/02.

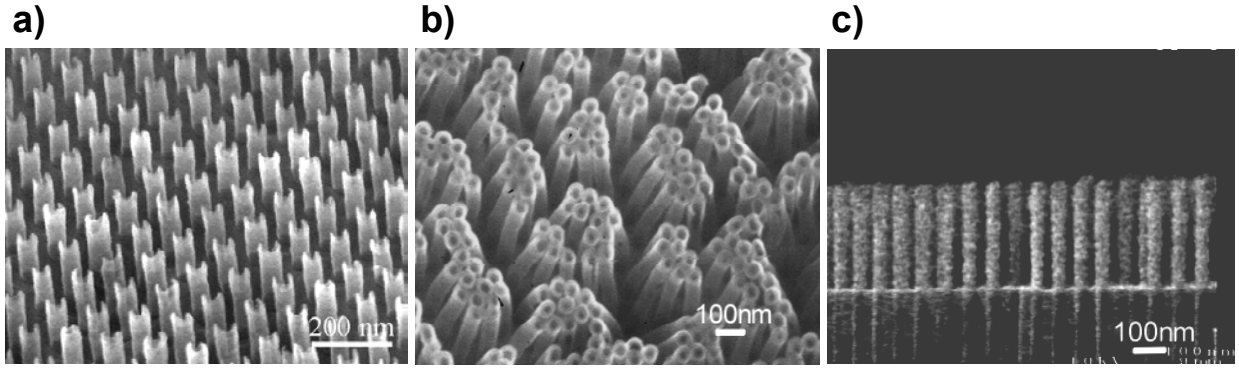

Fig.1 SEM images of exposed CNT arrays produced by etching back the alumina nanopore template. a) Nanotubes ~200 nm long exposed by ion milling. b) Sticking tubes after conventional wet etch of alumina. c) Non-sticking 500 nm long exposed tubes produced with dispersant added to etch solution. Here the tubes have a 25 nm Au/Pt coating (J. Xu et al., Brown U.).

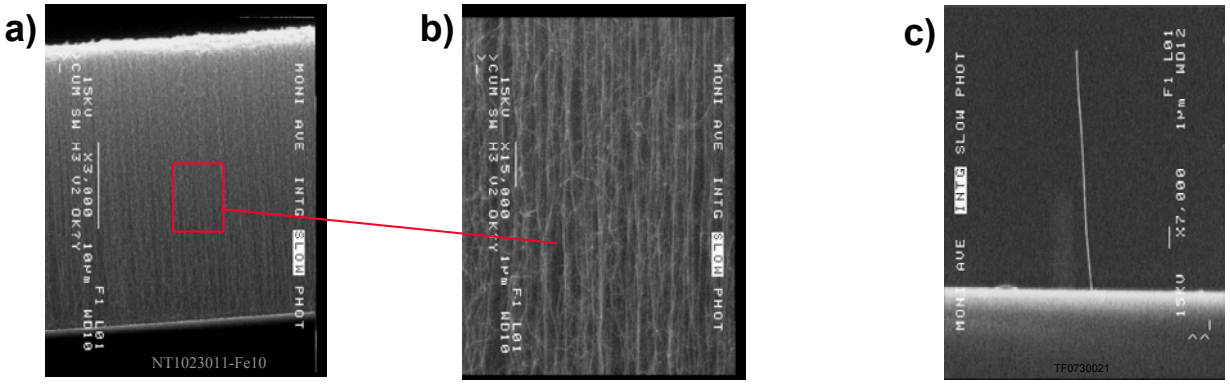

Figure 2. Nanotube growth on thin Fe catalysts using CVD. a) PECVD growth at 635°C with ethylene: low magnification SEM image showing dense growth of ~30μm long CNT. b) Higher magnification view showing local bending of nanotubes due to defect incorporation during this low temperature growth. c) SEM micrograph showing side view of a single, straight, *freestanding vertical nanotube* produced by 900°C methane CVD with a sub-nm Fe catalyst layer.

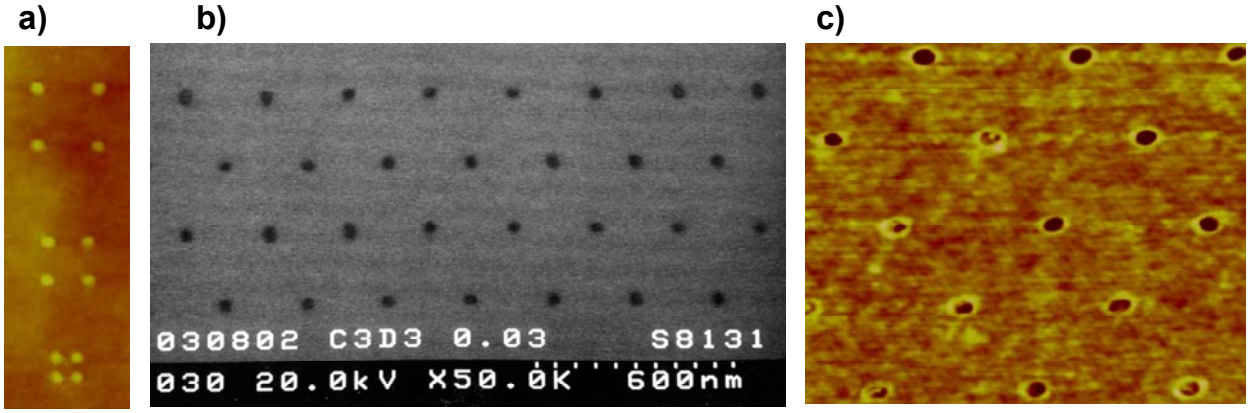

Figure 3. Catalyst patterns defined by electron beam lithography. a) AFM image of 8 nm thick Fe dots, ~50 nm in diameter, patterned by liftoff; b) SEM picture of 30 nm diameter pores, 10 nm deep with 2 nm thick Fe layers in the holes, patterned by reactive ion etching of SiO_2, followed by deposition and liftoff of Fe; c) AFM image of Fe-containing pores.